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Transformation of a Monotropic Mesophase into an Enantiotropic Mesophase  
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Constitutional Isomeric Mesogenic Side Groups

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ABSTRACT: The synthesis and the mesomorphic behavior of poly(methylsiloxane)s containing 4-methoxy-4'-hydroxy-trans- $\alpha$ -methylstilbene (4-n-PS) and 4-hydroxy-4'-methoxy-trans- $\alpha$ -methylstilbene (4'-n-PS) connected to the backbone by flexible spacers containing three, six and eleven ( $n = 3, 6, 11$ ) methylene units, and of some copolymers based on these two constitutional isomeric mesogenic side groups [4,4'(A/B)-n-coPS] is described. The copolymers derived from structural units whose homopolymers displayed enantiotropic mesophases [4,4'(A/B)-3-coPS and 4,4'(A/B)-11-coPS] exhibited a depression of both mesomorphic and crystalline phase transition temperatures. However, the 4,4'(50/50)-6-coPS copolymers, derived from structural units whose homopolymers (4-6-PS and 4'-6-PS) displayed nematic monotropic mesophases, exhibited an enantiotropic nematic mesophase.



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In a series of publications from our laboratory<sup>1-3</sup>, we have suggested that copolymerization of monomer pairs containing mesogenic units which are constitutional isomers should depress the tendency towards side-chain crystallization of polymers containing long flexible spacers and simultaneously provide qualitative information about the degree of decoupling. The previous experiments were performed with side groups based on 4-methoxy-4'-hydroxy-trans- $\alpha$ -methylstilbene (4-MHMS) and 4-hydroxy-4'-methoxy-trans- $\alpha$ -methylstilbene (4'-MHMS) constitutional isomers. However, all comonomer compositions were directly synthesized as mixtures of constitutional isomers by the monomethylation of 4,4'-dihydroxy-trans- $\alpha$ -methylstilbene<sup>1-3</sup>. Although the molar ratio between the two constitutional isomeric side groups was determined by spectroscopic methods, no information about the behavior of each of the two individual homopolymers based only on one individual constitutional isomer was available. Meanwhile we have synthesized and characterized the homopolymers based on 4-MHMS<sup>4</sup> and 4'-MHMS<sup>5</sup> individual isomers.

This paper describes the first quantitative results concerning the influence of copolymer composition on the phase transitions of thermotropic liquid crystalline poly(methylsiloxane)s containing 4-MHMS (4-n-PS), 4'-MHMS (4'-n-PS), and different ratios between these two constitutional isomeric mesogenic side groups [4,4'-(A/B)-n-coPS] attached to the polymer backbone through flexible spacers containing three, six and eleven methylenic units (Scheme 1). Ratio A/B refers to the molar ratio between 4-MHMS and 4'-MHMS constitutional isomeric side groups in copolymer.

The synthesis and characterization of these homopolymers and copolymers was performed according to general procedures used in our laboratory<sup>3-6</sup>. Copolymers based on several different ratios between the two individually synthesized isomeric monomers<sup>4,5</sup> were synthesized. Phase transitions were assigned by a combination of differential scanning calorimetry (DSC) (20°C/min) and thermal optical microscopy. DSC curves of all polymers were perfectly reproducible and independent of the heating or cooling scans that they were recorded from.

Figure 1 presents the phase diagram of the copolymer system 4,4'(A/B)-3-coPS. Both homopolymers exhibit an enantiotropic nematic mesophase and side chain crystallization<sup>4,5</sup>. The use of different ratios of these two constitutional isomeric side groups in the structure of 4,4'(A/B)-3-coPS depresses to approximately equal extent both the nematic-isotropic and the crystalline-nematic (as well as their reverse) phase transition temperatures. The enthalpy changes associated with the mesomorphic-isotropic and the reverse phase transitions of the homopolymers 4'-n-PS are equal to those of the 4-n-PS (n=3, 6, 11) and within experimental error are equal to those of their copolymers. For polymers with n=3,  $\Delta H_{in}=0.10$  kcal/mru, for n=6,  $\Delta H_{in}=0.09$  kcal/mru, while for polymers with n=11,  $\Delta H_{is}=0.75$  kcal/mru.

Figure 2 presents the phase diagram of the copolymer system 4,4'(A/B)-11-coPS. Both 4-11-PS and 4'-11-PS present an enantiotropic smectic mesophase and side chain crystallization<sup>4,5</sup>. The resulting copolymers exhibit a strongly depressed crystalline melting transition temperature and a slightly lowered smectic-isotropic transition temperature. As a consequence, copolymerization of the two constitutional isomeric mesogenic groups with long spacers enlarges the thermal stability of the mesophase. Interestingly, 4,4'(A/B)-11-coPS copolymers display three meltings, which as previously speculated, can be definitively assigned to the meltings of each of the two constitutional isomers and to their eutectic mixture respectively<sup>3</sup>. These independent meltings demonstrate a higher degree of decoupling of the side groups attached to the polymer backbone through long flexible spacers than that observed for copolymers with similar groups attached through short spacers.

Figure 3 a and b presents DSC curves describing the phase behavior of the most interesting copolymer: 4,4'(50/50)-6-coPS. 4-6-PS (Figure 3a, A and Figure 3b, A) and 4'-6-PS (Figure 3a, B and 3b, B) homopolymers each display a monotropic nematic mesophase. Upon copolymerization, both the crystalline phase and the nematic mesophase are strongly depressed (Figure 3a, C and 3b, C). However, as with

4,4'(A/B)-11-coPS, the crystalline phase is suppressed more than the liquid crystalline phase. Consequently, in this particular situation, copolymerization of the two constitutional isomeric monomers transforms the monotropic mesophase into an enantiotropic one. This last copolymer example demonstrates that constitutional isomeric mesogenic side groups drastically affect mesomorphic phase transitions in side chain liquid crystalline copolymers. A representative optical polarization micrograph showing the crystallization from the Schlieren nematic monotropic mesophase of 4'-6-PS is shown in Figure 4a. Figure 4b presents the Schlieren nematic texture of the enantiotropic mesophase displayed by 4,4'(50/50)-6-coPS.

Transformation of a monotropic mesophase into an enantiotropic mesophase by copolymerization is well documented in the case of main chain liquid crystalline copolymers<sup>7</sup>. The same effect was also observed upon increasing the main chain liquid crystalline polymer molecular weight<sup>7</sup>. In the case of side chain liquid crystalline polymers, transformation of virtual or monotropic mesophases into enantiotropic mesophases was mostly observed upon increasing the polymer molecular weight<sup>8</sup>, or on changing the nature of the polymer backbone<sup>3-5</sup>. This dependence between mesomorphic phase transition and copolymer composition does not yet elucidate a general relationship or trend in the case of the side chain liquid crystal copolymers<sup>9</sup>. In most cases and as in the examples detailed here, mesomorphic transitions are strongly depressed upon copolymerization<sup>9,10</sup>. This is in contrast to main chain liquid crystalline polymers where mesomorphic phase transitions and the corresponding thermodynamic parameters are weight averaged values of the corresponding parameters of the parent homopolymers<sup>11</sup>.

In conclusion, although copolymerization of side chain liquid crystalline mesogenic monomers still provides an open subject of research, the experiments described in this communication demonstrate the ability to tailor mesomorphic phase transitions using copolymers based on constitutional isomeric mesogenic units.

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### Figure and Scheme Captions

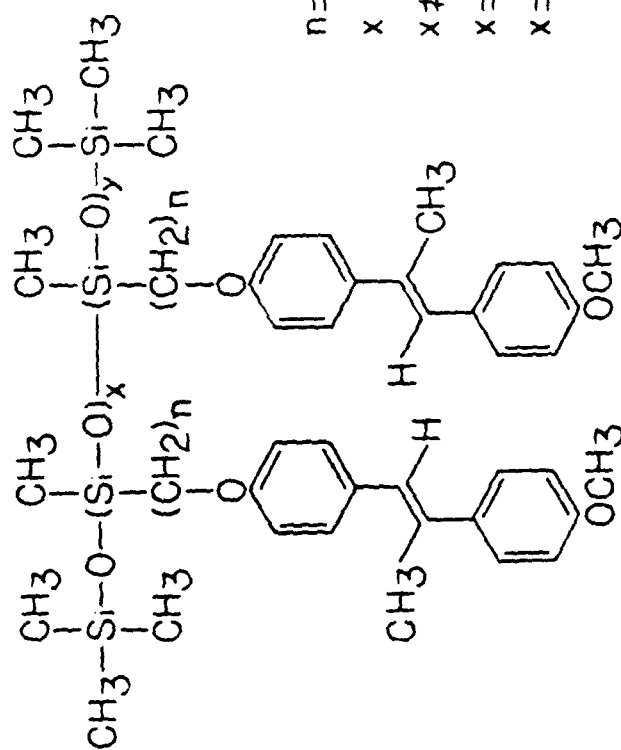
Figure 1: The dependence between: ( $\Delta$ ,  $T_{kn}$ ) crystalline-nematic; ( $\blacktriangle$ ,  $T_{nk}$ ) nematic-crystalline; ( $O$ ,  $T_{ni}$ ) nematic-isotropic; and ( $\bullet$ ,  $T_{in}$ ) isotropic-nematic transition temperatures and the 4,4'(A/B)-3-coPS copolymer composition.

Figure 2: The dependence between: ( $\Delta$ ,  $T_{ks}$ ) crystalline-smectic; ( $\blacktriangle$ ,  $T_{sk}$ ) smectic-crystalline; ( $O$ ,  $T_{si}$ ) smectic-isotropic; and ( $\bullet$ ,  $T_{is}$ ) isotropic-smectic transition temperatures and the 4,4'(A/B)-11-coPS copolymer composition.

Figure 3: a) Normalized DSC second heating scan traces ( $20^{\circ}\text{C}/\text{min}$ ) of: A) 4-6-PS; B) 4'-6-PS; C) 4,4'(50/50)-6-coPS; and b) Normalized DSC first cooling scan traces ( $20^{\circ}\text{C}/\text{min}$ ) of: A) 4-6-PS, 4'-6-PS; C) 4,4'(50/50)-6-coPS.

Figure 4: Representative optical polarized micrographs (100X) of: a) 4'-6-PS after 3 min of annealing at  $105^{\circ}\text{C}$  on cooling from the isotropic phase; b) 4,4'(50/50)-6-coPS after 3 min of annealing at  $69^{\circ}\text{C}$  on the cooling scan.

Scheme 1: Poly- and copoly(methylsiloxane)s containing 4-MHMS and 4'-MHMS based mesogenic side groups and different spacer lengths.



$n = 3, 6, 11$

$x + y = 100$

$x \neq 0 ; y \neq 0 : 4, 4'(\text{A/B})\text{-}n\text{-coPS}$

$x = 0 ; y = 100 : 4'\text{-}n\text{-PS}$

$x = 100 ; y = 0 : 4\text{-}n\text{-PS}$

Scheme 1

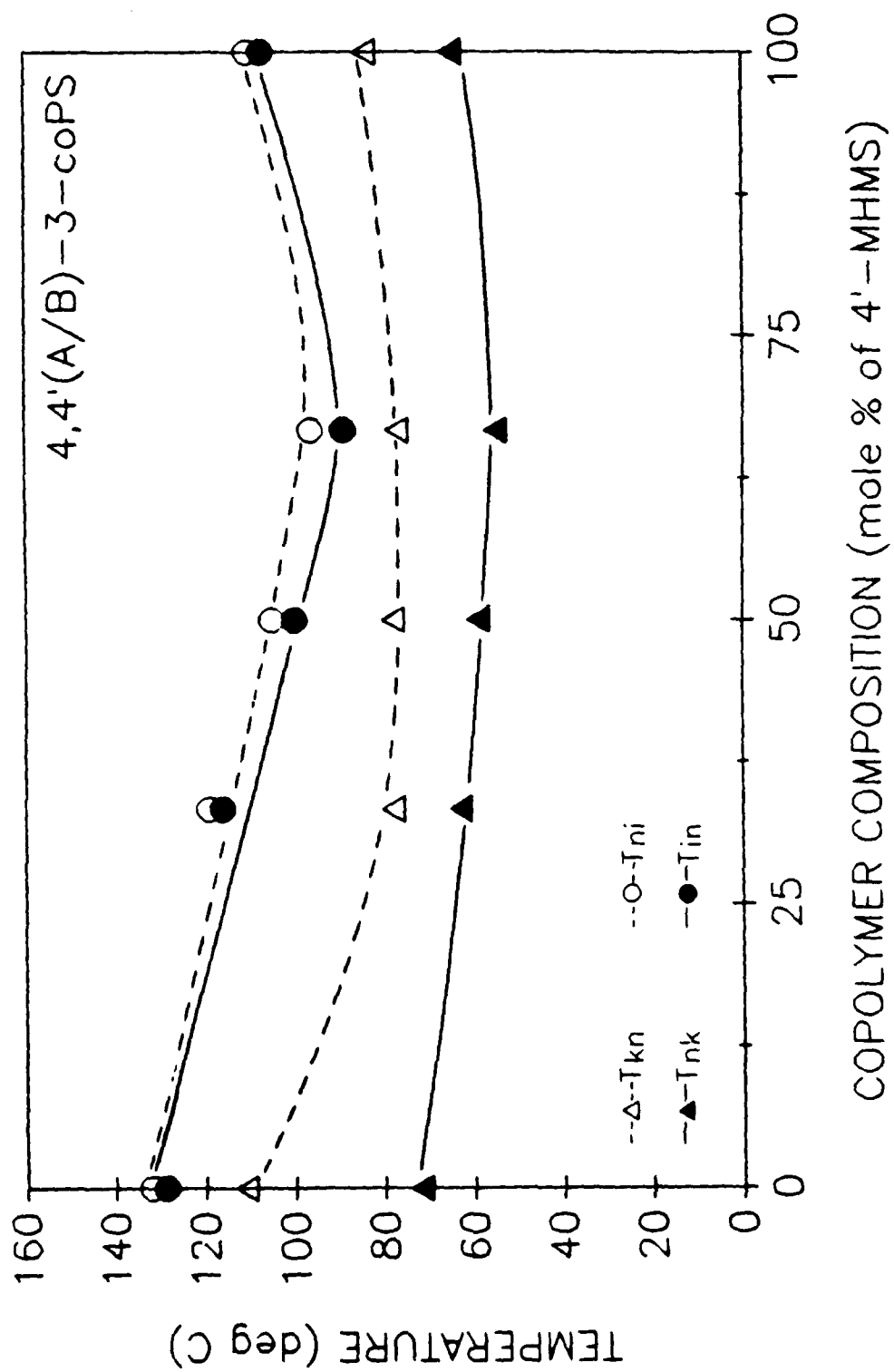


Figure 1

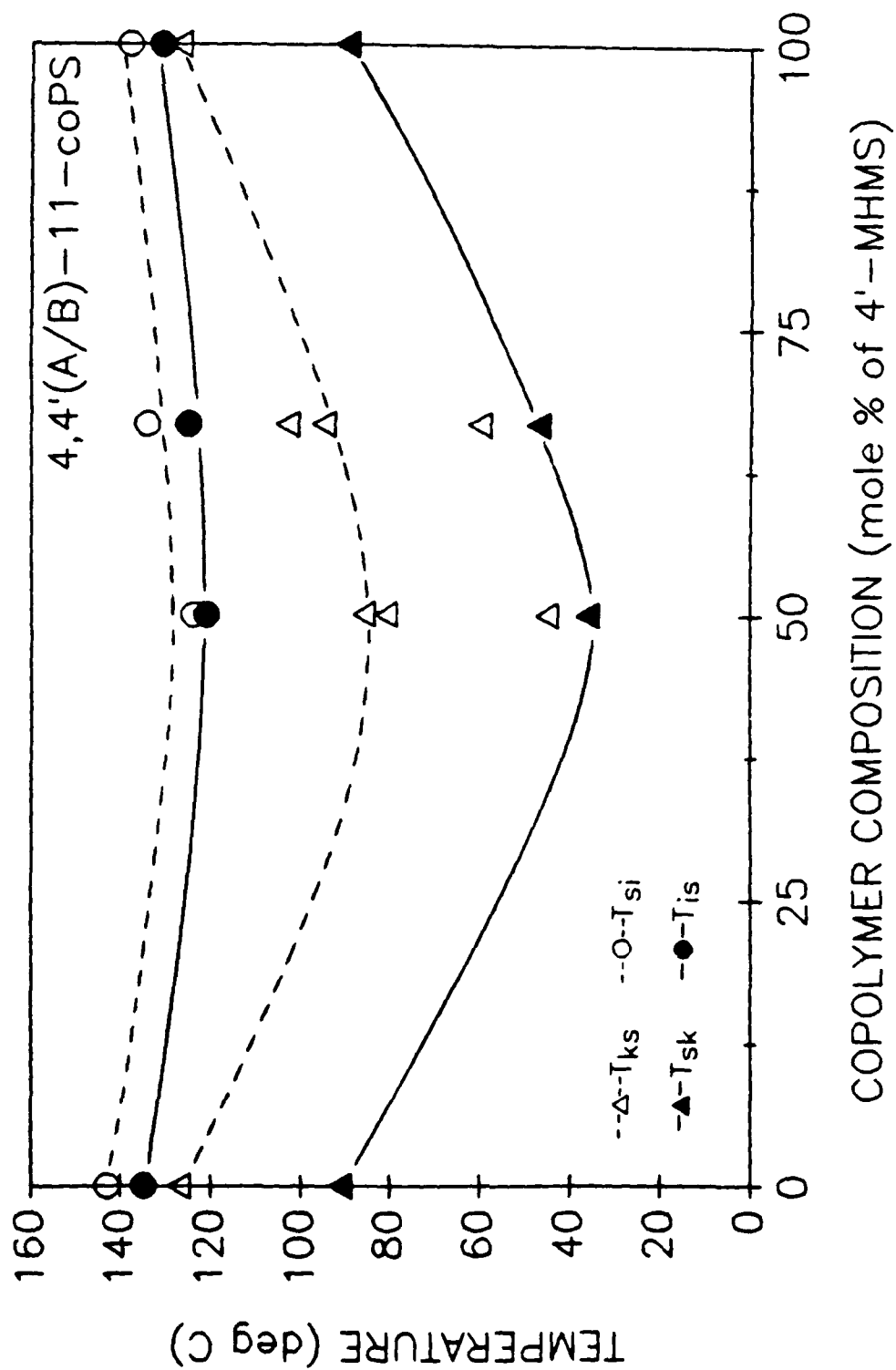
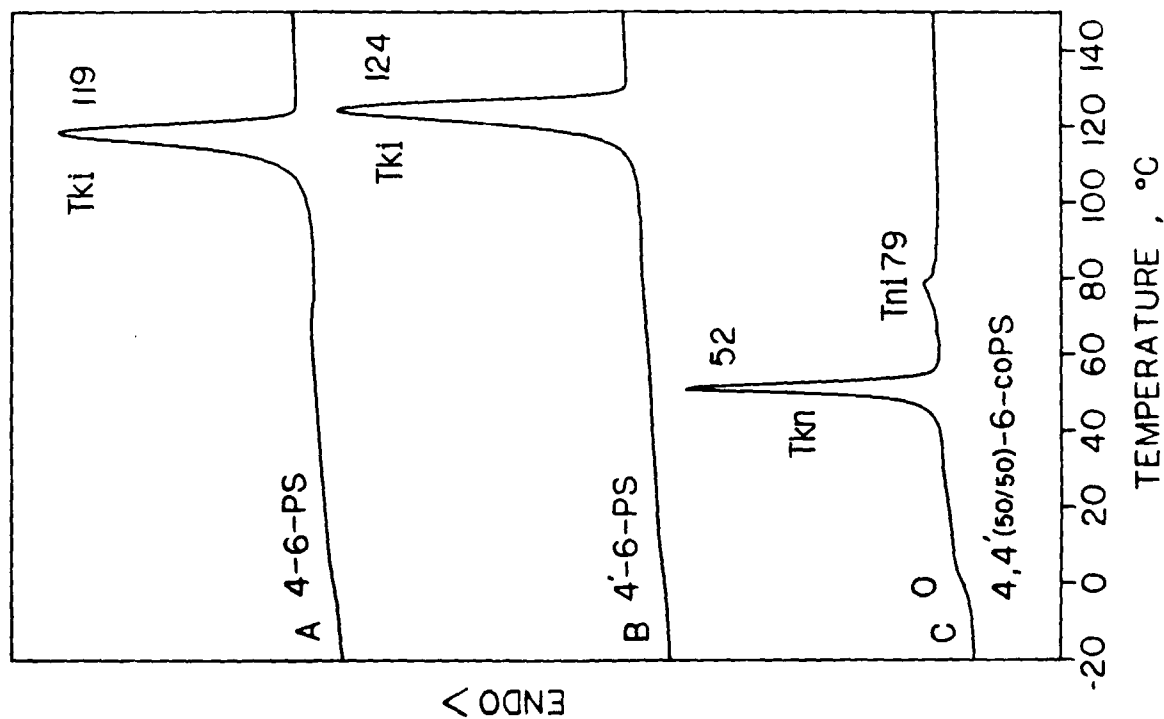


Figure 2

a



b

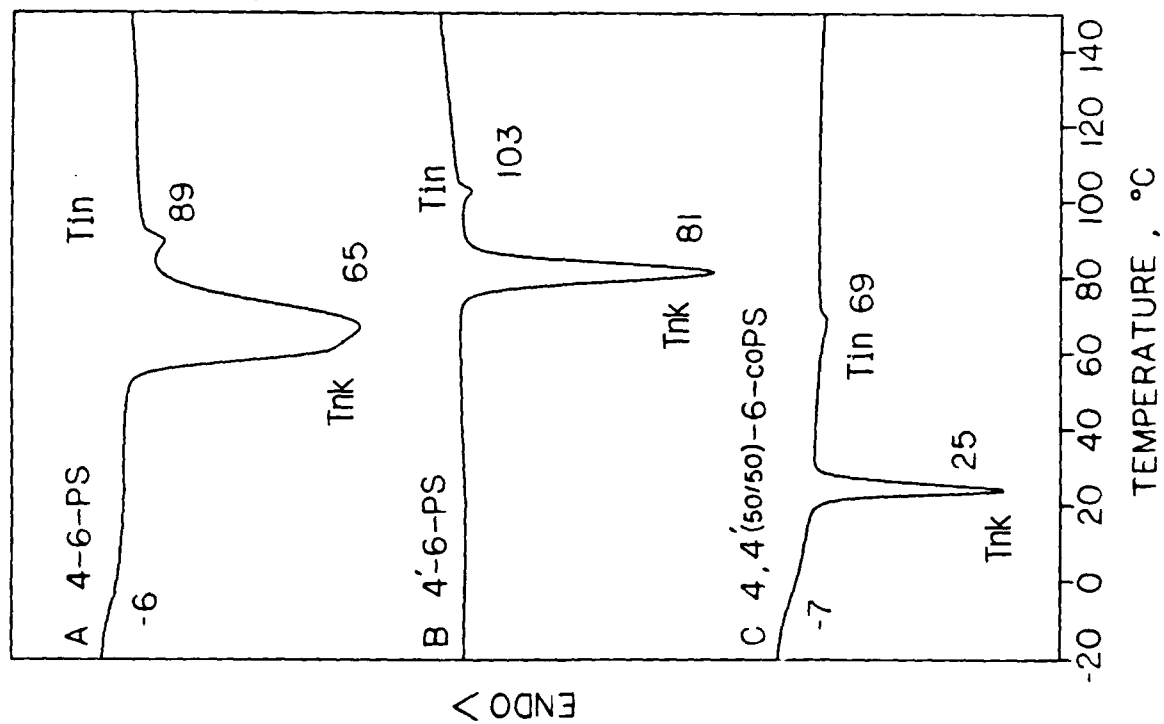


Figure 3

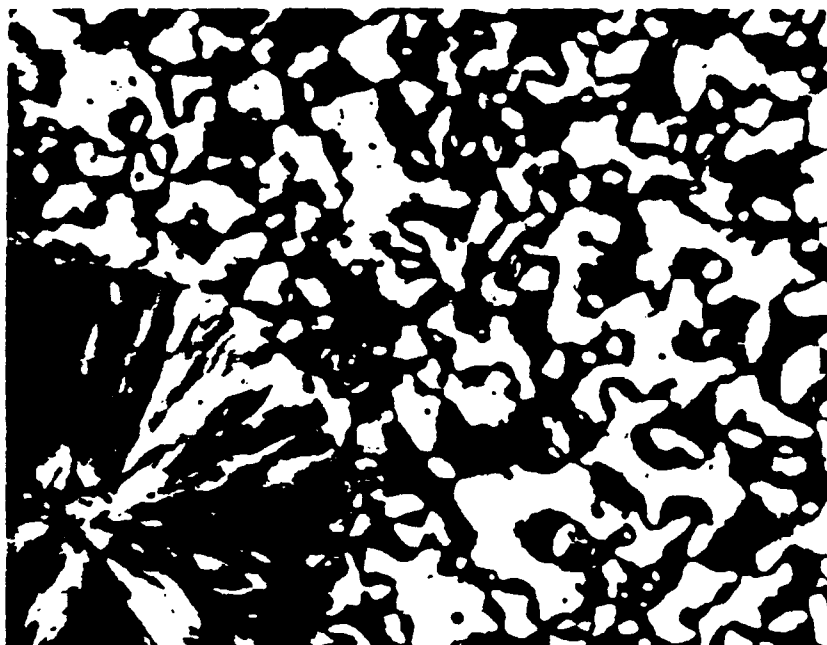


Figure 4a

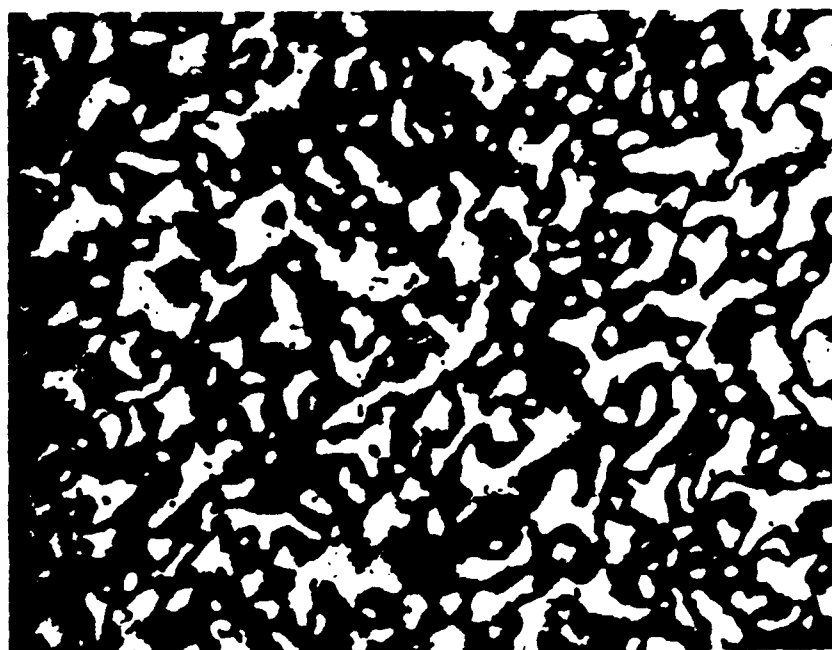


Figure 4b